II. "On the Specific Heat and other physical properties of Aqueous Mixtures and Solutions." By A. Dupré, Ph.D., Lecturer on Chemistry at the Westminster Hospital, and F. J. M. Page. Communicated by C. Brooke, F.R.S. Received February 4, 1869.

(Abstract.)

Part I.

Mixtures of Ethylic Alcohol and Water.

Section 1. *Specific Heat.*

For the methods employed in estimating the specific heat of these mixtures, see a former abstract, 'Proceedings of the Royal Society,' vol. xvi. p. 336.

In the present paper the authors give the specific heat of an additional number of mixtures, so as to complete the series for every 10 per cent. from water to absolute alcohol.

The following Table gives the mean of the results obtained in all experiments, details of seventy-four of which are given :—

Percentage of alcohol, by weight.	Specific heat found.	Specific heat calculated.	Difference.
5	101·502	.....	.....
10	103·576	96·043	+ 7·533
20	104·362	92·086	12·276
30	102·602	88·129	14·473
40	96·805	84·172	12·633
45	94·192	82·193	11·999
50	90·633	80·215	10·418
60	84·332	76·258	8·074
70	78·445	72·301	6·144
80	71·690	68·344	3·346
90	65·764	64·387	1·377
100	60·430	.....	.....

Section 2. *Heat produced by the mixing of Alcohol and Water.*

This was estimated as follows :—The liquid which formed the smallest portion of the mixture was sealed up in a thin glass bulb ; this was then introduced into the calorimeter, the glass bulb was broken, the mixture formed, and the rise in the temperature of the calorimeter observed.

The units of heat evolved in the formation of 5 grms. of each mixture were thus calculated, and found to be—

10 per cent. spirit	26·6850	50 per cent. spirit	35·5850
20 „ „	43·9545	60 „ „	27·2620
30 „ „	47·9800	70 „ „	18·8200
40 „ „	44·8630	80 „ „	12·4775
45 „ „	38·8095	90 „ „	7·7025

Section 3. *Boiling-points.*

A small flask was taken ; into this 100 cub. centims. of the mixture was

introduced, and the mouth of the flask closed by a doubly perforated cork. Into one of these perforations a thermometer was introduced, into the other a bent tube, dipping beneath the surface of the liquid in the flask, and connected at its other extremity with a Liebig condenser. This tube had a lateral opening (inside the flask) just beneath the cork; by means of this the vapour escaped to the condenser, and trickled back into the flask after being condensed. Thus the composition of the mixture was retained as uniform as possible. Thus estimated, the barometer standing at 744·4 millims., the boiling-points are given in the following Table.

Percentage of alcohol, by weight.	Boiling-point observed.	Boiling-point calculated*.	Difference.
0	99·4	.....	.....
10	90·98	97·25	−6·27
20	86·50	95·10	−8·60
30	84·01	92·95	−8·94
40	82·52	90·90	−8·38
45	81·99	89·72	−7·73
50	81·33	88·60	−7·27
60	80·47	86·50	−6·03
70	79·61	84·35	−4·74
80	78·84	82·20	−3·36
90	78·01	80·05	−2·04
100	77·89	.....	.....

Section 4. *Capillary Attraction.*

This was estimated by carefully observing the heights to which the several mixtures rose in a capillary tube 0·584 millim. in diameter.

These heights were measured by means of a telescope and a millimetre-scale etched on a glass rod. This glass rod was fixed to the capillary tube, and terminated at its lower extremity in a point, which was made just to touch the surface of the liquid.

Several precautions were necessary to render the measurements accurate.

The results are contained in the following Table:—

Percentage of alcohol, by weight.	Height, assuming water = 100 millims.	Relative molecular attraction.	Height calculated.	Difference.
0	100·00	100·00	100·00	.....
10	69·17	68·07	93·11	−25·04
20	56·43	54·83	86·22	−31·39
30	48·19	46·15	79·34	−33·19
40	45·30	42·56	72·45	−29·89
45	43·74	40·64	69·00	−28·36
50	42·93	39·43	65·56	−26·13
60	42·30	37·89	58·68	−20·79
70	41·76	36·42	51·79	−15·37
80	41·29	35·03	44·90	− 9·87
90	40·54	33·35	38·02	− 4·67
100	39·21	31·13	31·13	.....

The third column gives the length of a column of water equal in weight

* Calculated on the assumption that the alcohol and water in a mixture have an influence on the boiling-point of the mixture proportional to their respective weights.

to the thread of alcoholic mixture contained in the second column, and gives, therefore, a measure of the relative strength of the molecular attraction in the various mixtures.

The experiments were made at a temperature of 16° C.

Section 5. *Rate of Expansion.*

This was determined by estimating the specific gravity of the different mixtures at the temperatures 10° C., 15°·5 C., 20° C.

The specific-gravity bottle has two necks; into one was fitted a thermometer with a long bulb, whilst the other ended in a capillary tube.

This bottle was placed in a water-bath, whose temperature was under perfect control, and thus the specific gravity could be accurately estimated at the above-named temperatures.

Section 6. *Compressibility.*

This property was estimated by an apparatus similar to the one employed by Regnault and Grassi, but of simpler construction.

The piezometer was of glass; pressure was applied to the inside and outside by forcing air into the apparatus by means of a small pump; 0·000002 was always added as a correction for the compressibility of the piezometer.

The two following Tables give the results obtained in Sections 5 and 6.

Percentage of alcohol, by weight.	Volume at 10° C.	Volume at 20° C., found.	Volume at 20° C., calculated.	Difference.
0	100	100·154	100·154	.....
10	100	100·212	100·272	−·060
20	100	100·405	100·386	+·019
30	100	100·632	100·498	+·134
40	100	100·783	100·601	+·182
45	100	100·827	100·652	+·175
50	100	100·868	100·700	+·168
59·77	100	100·914	100·789	+·125
69·73	100	100·980	100·874	+·106
79·81	100	101·020	100·954	+·066
89·89	100	101·052	101·034	+·018
100·00	100	101·088	101·088	.....

Percentage of alcol ol, by weight.	Compressibility for one atmosphere, found.	Compressibility for one atmosphere, calculated.	Difference.
0	0·00004774	0·00004774	.....
10	0·00004351	0·00005387	0·00001036
20	0·00003911	0·00005998	0·00002087
30	0·00003902	0·00006584	0·00002682
40	0·00004347	0·00007118	0·00002771
45	0·00004608	0·00007366	0·00002758
50	0·00004878	0·00007600	0·00002722
59·77	0·00005620	0·00008029	0·00002409
69·73	0·00006159	0·00008426	0·00002267
78·81	0·00006942	0·00008775	0·00001833
89·89	0·00007950	0·00009140	0·00001190
100·00	0·00009349	0·00009349	.....

Weight of water contained in the piezometer 114·9727 grms.

In conclusion the authors confine themselves to pointing out certain relations which connect the various physical properties examined.

These properties may be divided into two classes, according as they reach a maximum deviation from the theoretical mean at 30 per cent. or 40 per cent.; each of these is divided into two subclasses, one containing those properties in which the numbers found are above those calculated, and the other containing those in which they are below.

Class I.

Subclass *a*. Specific heat.
Heat produced by mixing.
,, *b*. Boiling-point.
Capillary attraction.

Class II.

Subclass *c*. Rate of expansion.
,, *d*. Compressibility.

Other characters, examined by previous investigators, are :—

1. *Vapour-tension*: this falls under Class I. Subclass *b*.
2. *Specific Gravity*.
3. *Index of Refraction*.

The two latter form a new class, coming to a maximum deviation from their theoretical value at 45 per cent.

In subclass *a*, specific heat—by reference to the Tables given, it will be seen that the first addition of alcohol to water (though alcohol has a specific heat much lower than that of water) produces mixtures which have a higher specific heat than water, and that a mixture containing between 30 and 40 per cent. alcohol has the same specific heat as water.

Similarly alcohol, though much more compressible than water, yet, when added to it, forms mixtures less compressible than water; so that a mixture containing between 45 and 50 per cent. alcohol has the same compressibility as water.

The rate of expansion is remarkable, as, starting from water, it at first is below the theoretical value, then rises; at 17 to 18 per cent. the rate of expansion is identical with the calculated expansion; for all mixtures stronger than this, the rate of expansion is constantly above that calculated.

The whole of the physical characters of mixtures of alcohol and water come to a maximum deviation from their theoretical values somewhere between 30 per cent. and 45 per cent. alcohol by weight. The 30 per cent. nearly corresponds to the formula $C_2 H_6 O + 6 O H_2$ (=29·87 per cent.);

the 45 per cent. has approximately the formula $C_2 H_6 O + 3 O H_2$ (=46 per cent.).

Some of the physical properties examined seem to be especially connected with each other; these are:—

1. Specific heat and heat produced by mixing; for by dividing the number of units of heat evolved by 5 grammes of any mixture by 3·411, the elevation of the specific heat of such mixture above the theoretical specific heat is obtained.
2. Boiling-point and capillary attraction; by dividing the depression of the capillary attraction by 3·6, the depression of the boiling-point is obtained.

Deville & Hoek have shown the specific gravity and index of refraction to be connected with each other (Ann. de Chim. et de Physique, 3rd ser. vol. v. Pogg. Ann. vol. cxii.).

Whether the relations thus established between the various physical properties of alcoholic mixtures hold good with other similar substances, or whether these mixtures form a singular exception, must be decided by further research.

March 18, 1869.

Dr. WILLIAM ALLEN MILLER, Treasurer and Vice-President, in the Chair.

The following communications were read:—

I. "Researches into the Chemical Constitution of Narcotine, and of its Products of Decomposition."—Part III. By A. MATTHIESSEN, F.R.S., Lecturer on Chemistry in St. Bartholomew's Hospital. Received February 18, 1869.

(Abstract.)

In this part the preparation is described of two new bases derived from narcotine.

1. *On the Action of Hydriodic Acid on Narcotine.*—When narcotine is heated with fuming hydriodic acid, iodide of methyl is evolved, and on investigating the residue it is found to consist of the iodide of a new base.

In two experiments made with 50 grms. of narcotine, 45·7 and 46·2 grms. of iodide of methyl, and in a third experiment with 100 grms. of narcotine, 91·8 grms. of iodide of methyl, were obtained, 51·5 grms. and 103·1 grms. being the theoretical quantity required for the following reaction:—

$$C_{22} H_{23} N O_7 + 3 HI = C_{19} H_{17} N O_7 + 3 CH_3 I.$$